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CURE ANALYSIS OF AN ADHESIVE PRIMER

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PDO 6985008, Topical Report

J. M. Hubach, Project Leader

Project Team:
F. E. Meisner

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Prepared for the United States Energy Research and Development Administration Under Contract Number EY-76-C-04-0613 USERDA

Bendix Kansas City Division

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Communications Services Bendix Kansas City Division

CURE ANALYSIS OF AN ADHESIVE PRIMER

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Prepared by J. M. Hubach, D/814, under PDO 6985008

An optimal cure schedule for BR-125 adhesive primer was determined using the Audrey II, System 300 Dielectric Analyzer. Data from T-Peel tests are included which confirm the cure schedule predicted by the Audrey II.

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SUMMARY

Selection of a cure cycle is generally based on the results of extensive physical properties tests. The advent of dielectric analysis provides the means of accurately predicting cure schedules without this extensive testing.

Dielectric analysis is based on the reaction of the dipoles within a polymer to an alternating electric field. As the field alternates the dipoles attempt to swivel in step but are restricted because of their relatively fixed position within the polymeric structure. Capacitance is the measure of the dipole's ability to align and dissipation is the power lost in alignment.

For a thermosetting polymer, dissipation versus time curves provide an insight into the curing mechanism and can be correlated to known physical and chemical changes. The dissipation versus temperature curves provide a fingerprint of the curing polymer and extent of cure.

The material evaluated in this study was BR-125 adhesive primer, a modified nitrile epoxy supplied by the Bloomingdale Division of American Cyanamid. Our application involved a special use of the primer as an adhesive which necessitated an alternative cure schedule.

Typical curves of dissipation as a function of either time or temperature are shown. As a result of these curves, a minimum cure temperature was determined as well as an optimum cure cycle.

T-Peel specimens were used to show that the alternate cure cycle suggested by the Audrey data was equivalent to the manufacturer's recommended cure and that the prediction of minimum cure temperature was also valid.

DISCUSSION

SCOPE AND PURPOSE

The purpose of this study was to optimize the cure schedule of an adhesive. The Audrey II Dielectric Analyzer was used to predict dielectrically both the optimum cure time and temperature. These conclusions were then confirmed using data from T-Peel tests.

ACTIVITY

Test Definition

Each thermosetting adhesive has a specific cure cycle or cycles recommended by the manufacturer. Occasionally the need exists to modify the recommended schedule because of time or temperature limitations or other external circumstances. Prior to the use of dielectric analysis, cure cycle modification was based on a combination of trial and error and extensive physical properties testing. Both are costly, time consuming processes, and ill suited to a short term solution of production problems. Dielectric analysis, coupled with a minor amount of physical properties testing, can establish an alternate cure cycle while conserving both time and money.

Dielectric analysis is based on the intrinsic dielectric response of a polymeric material; this is the reaction of the dipoles within a polymer to an alternating electric field. These dipoles may be created artificially by charges collecting on anomalies within the material (interfacial polarization) or by unbalanced charge distribution within the molecule (orientational polarization). In either case, the dipoles attempt to align themselves with the electric field. As the field alternates the dipoles attempt to swivel in step but are restricted because of their relatively fixed position within the polymeric structure. Capacitance can be described as a measure of the ability to align whereas dissipation is the power lost in alignment attempts. Thus the current leads the voltage and is attenuated. Both the dissipation and capacitance of a polymer are affected by viscosity, molecular weight, and the frequency of the alternating field. Molecular weight and viscosity relate directly to restricted dipole movement. If the frequency of the alternating field is too high, the dipoles within the material cannot move fast enough to respond to the changing field. Thermoplastic polymers have the simplest response patterns since the primary changes in these materials are caused by the effect of temperature on viscosity or thermal degradation on molecular weight. Thermosets have more complex responses because of the irreversible changes that take place during cure. Dipoles are created and disappear at the same time that viscosity and molecular weight are changing.

Test Methods

The equipment selected for monitoring the dielectric responses of polymers was the Audrey II, System 300 Dielectric Analyzer (Figure 1). The System 300 package consists of the Audrey II, the ATC-200 temperature controller, a Research Incorporated, Model 5310 Data-Trak card reader, the Di/An 300 test cell, and a modified Hewlett Packard RS-360 recorder. A Hewlett-Packard 7044-A recorder, an oscilloscope, and a Fred S. Carver Incorporated 12-ton (106.8 kN) laboratory press have also been added.

In order to accommodate the variety of polymeric materials, three different electrode designs may be used with the Audrey II: the capacitive pair, the indirect electrode, and the Monoprobe. The capacitive pair, shown in Figure 2, was selected for this study and can be disposable or permanent.

Two recorders were used to simplify data handling. One provided dissipation, capacitance, and temperature as a function of time, and the other gave dissipation or capacitance as a function of temperature. Although both dissipation and capacitance data were available, most data interpretation involve only the dissipation curves.

For a thermosetting polymer, dissipation versus time curves provide an insight into the curing mechanism and can be correlated to known physical and chemical changes. These curves are ideal for processing guides. The dissipation versus temperature curves can be used to obtain a fingerprint of the curing polymer and provide extent of cure information. This is done by monitoring dissipation versus temperature during several heat-up and cool-down cycles. The resultant circle curves indicate if any additional dielectric changes have occurred. If a material is fully cured at a given temperature, no additional changes can take place and heat-up and cool-down will be identical. However, if the material is heated above its initial cure temperature, additional cure or thermal degradation will occur which will alter the cool-down portion of the cycle and subsequent cycles. Using the circle curves as a guide, it should be possible to predict cure schedules without extensive physical properties testing.

The material evaluated in this study was BR-125 adhesive primer manufactured by the Bloomingdale Division of American Cyanamid. BR-125 primer is a modified nitrile epoxy normally used in conjunction with FM-123-2 film adhesive. However, our application

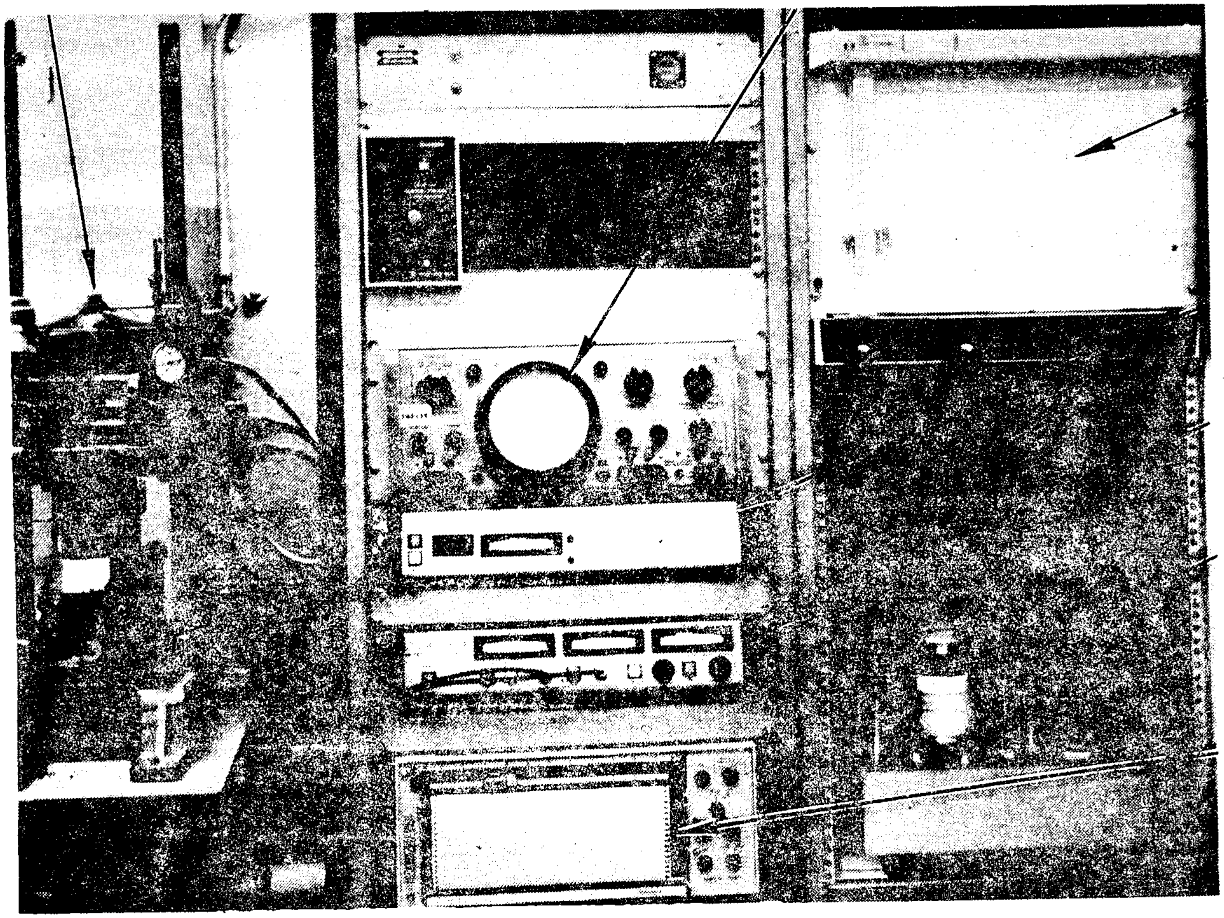

Figure 1. Equipment for Dielectric Analysis

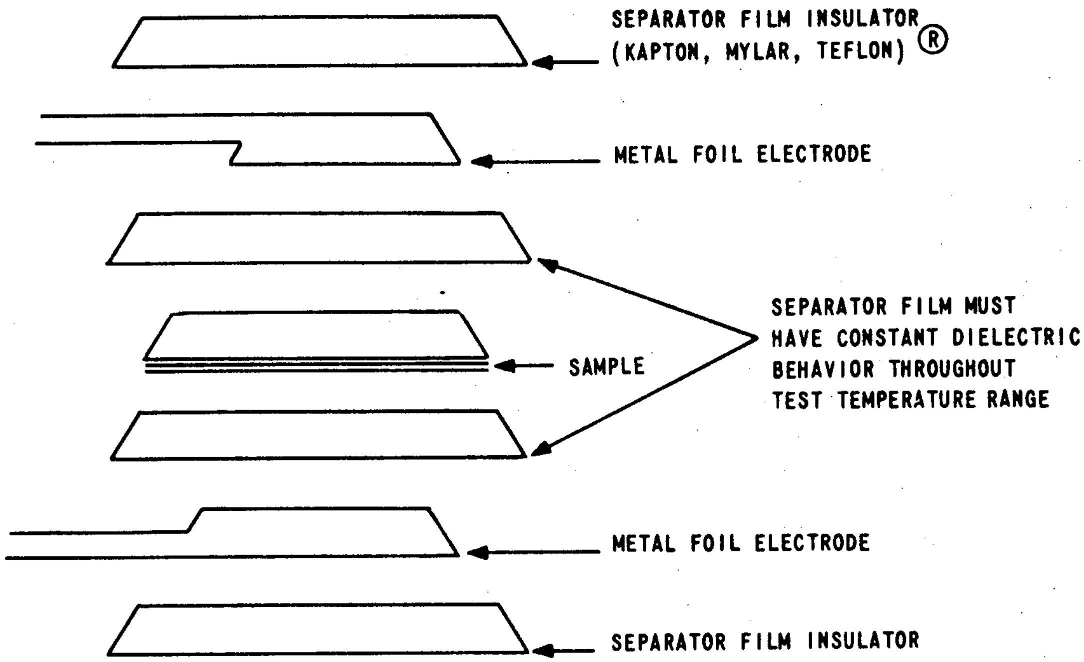

Figure 2. Capacitive Pair Electrodes

involved using the primer by itself as an adhesive capable of achieving a 5.08 to 12.7 μm (0.0002 to 0.0005 inch) thick bond line. Normally BR-125 is supplied as 5 percent solids in methyl ethyl ketone. For our application, the material is being supplied as a 50 percent solids solution which we dilute with acetone to give a final product that is approximately 8 percent solids.

The manufacturer's suggested cure schedule is given in Table 1. It has two drawbacks; it is time consuming and it is tied to the use of the film adhesive. The cure cycle used by our production area consisted of air drying for 1 hour plus 4 hours at 150°C. This cycle was producing acceptable parts but again the cycle was time consuming and was a definite candidate for optimization.

Audrey Analysis

The first step in the optimization process was to get a dielectric fingerprint of the curing material. This is done by monitoring the polymer during a controlled heat-up from ambient conditions. In all, nine runs were made on the BR-125.

Table 1. Application of Primer

Step	Conditions
1	Air dry for one hour minimum after brush or spray application.
2	Oven dry for 30 minutes at 66°C.
3	Apply adhesive film to primed parts.
4	Assemble, apply 345 kPa (50 psi) pressure and cure for 60 minutes to 107°C plus 90 minutes at 107°C.

An outline of the experimental conditions used to obtain the charts is presented in tabular form in Table 2. The first four specimens were tested without predrying. This was an unsatisfactory procedure because the unevaporated solvent interfered with the Audrey output and resolution of the dissipation curves was very poor. This was confirmed by the last two runs where additional solvent was deliberately added. Drying the primer, either in air or in vacuum prior to testing produced dissipation curves with improved resolution which lent themselves most readily to interpretation.

Typical dissipation as a function of time and dissipation as a function of temperature curves for the dried primer are shown in Figures 3 and 4. Since the dissipation was nonlinear, all values are given as chart divisions. Because of the difference in heat-up rates the dissipation/time curves appear to show a much wider variation than actually exists. These curves do show that, at either temperature, the material makes almost no change dielectrically after 30 minutes including the heat-up time. Consequently, after taking into account the small size of the sample used by the Audrey, a cure of 1 hour at 148°C with additional time predicated on the size of the bonding fixture was recommended. Either cure temperature was satisfactory but we recommended 148°C because the amplitude of the dissipation curve between 100 and 1000 Hz was somewhat lower suggesting a more tightly crosslinked polymer.

In addition, prior work with other materials suggested that the minimum dissipation value on the 100 hertz curve probably coincided with the temperature at which cure was initiated. From Figure 4, this temperature appears to be somewhere between 90° and 95°C. Apparently American Cyanamid has allowed for a 15° to 20°C cushion between their recommended cure temperature and the minimum.

Table 2. Experimental Conditions for Testing

Run Number	Special Conditions	Cure (°C)	Time at Temperature (Hours)
1	No air dry, undiluted	121	4
2	No air dry, undiluted	148	2
3	No air dry, undiluted	148	2
4	No air dry, undiluted	121	3
5	Air dry, 3 hours, undiluted	148	3
6	Air dry, 3 hours, undiluted	121	3
7	Vacuum dry, 3 minutes, undiluted	121	2
8	MEK* added	121	2
9	Trichloroethylene added	121	4

*Methyl ethyl ketone

Mechanical Tests

In order to confirm the conclusions obtained using dielectric analysis, four sets of five T-peel specimens were prepared using the same 0.102 mm (4 mil) thick Super Invar required in the production application of this adhesive. The cure conditions of each set are given in Table 3. Cure 1 was that recommended by the manufacturer and Cure 2 was the alternative cure predicted by the Audrey. The temperature for Cure 3 was selected because it was below the point where cure initiation was suspected. The correct cure temperature was selected for Cure 4 but the cure time was shortened. All of the strips of 101.6 by 25.4 mm (8 by 1 inch) Invar were solvent wiped with methyl ethyl ketone and then vapor degreased in trichloroethylene. The cleaned strips were then spray coated using three passes of the sprayer with dilute BR-125. After cure, the specimens were tested according to ASTM-D-1876 except that no preconditioning was used. The results of these T-Peel tests are given in Table 4. Cures 1 and 2 gave equivalent results confirming the predictions made by the Audrey dielectric analyzer. The results of Cures 3 and 4 also reaffirm the usefulness of dielectric analysis. In conjunction with the poor strengths, the surfaces of both of these sets of specimens were still tacky. This indicates that both sets were

Table 3. Cure Conditions

Cure	Time (Hours)	Conditions
1	1 0.5 1 1.5	Air dry plus at 66°C plus to 107°C plus at 107°C
2	1 1	Air dry plus at 148°C
3	1 0.5 1.5	Air dry plus at 65°C plus at 79°C
4	1 0.5 0.5 0.5	Air dry plus at 66°C plus to 107°C plus at 107°C

Table 4. Peel Strength

Set Number	Cure Condition	Number of Specimens	Peel Strength (N/cm Width)
1	1	5	13.7
2	2	4	13.1
3	3	4	7.5
4	4	5	10.8

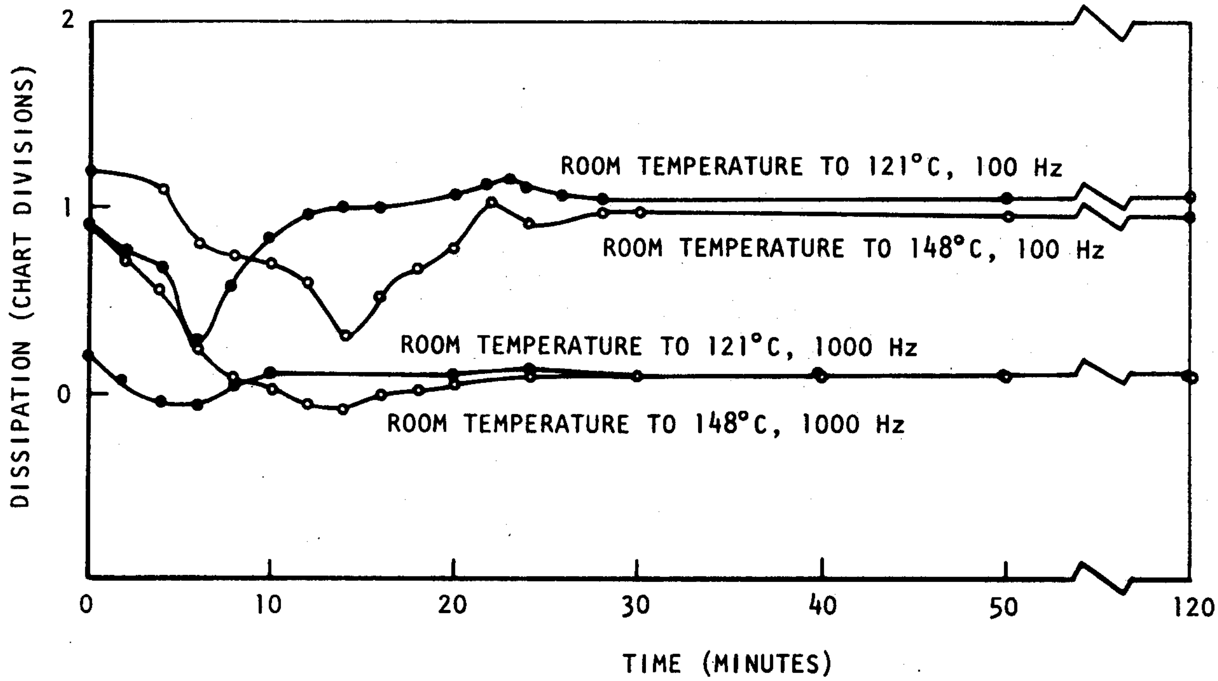

Figure 3. Nonlinear Dissipation in Chart Divisions as a Function of Time in Minutes for BR-125 Adhesive Primer

inadequately cured. Additional time at 107°C would have been sufficient to properly complete the cure of Set 4. However, it is doubtful if prolonged exposure to 79°C would have completed the cure of the third set.

ACCOMPLISHMENTS

The Audrey Dielectric Analyzer was used to successfully predict an alternate cure schedule for BR-125 adhesive primer. These predictions were then confirmed using T-Peel tests. In this manner, modifying cure schedules can be done on a more scientific basis than was previously available.

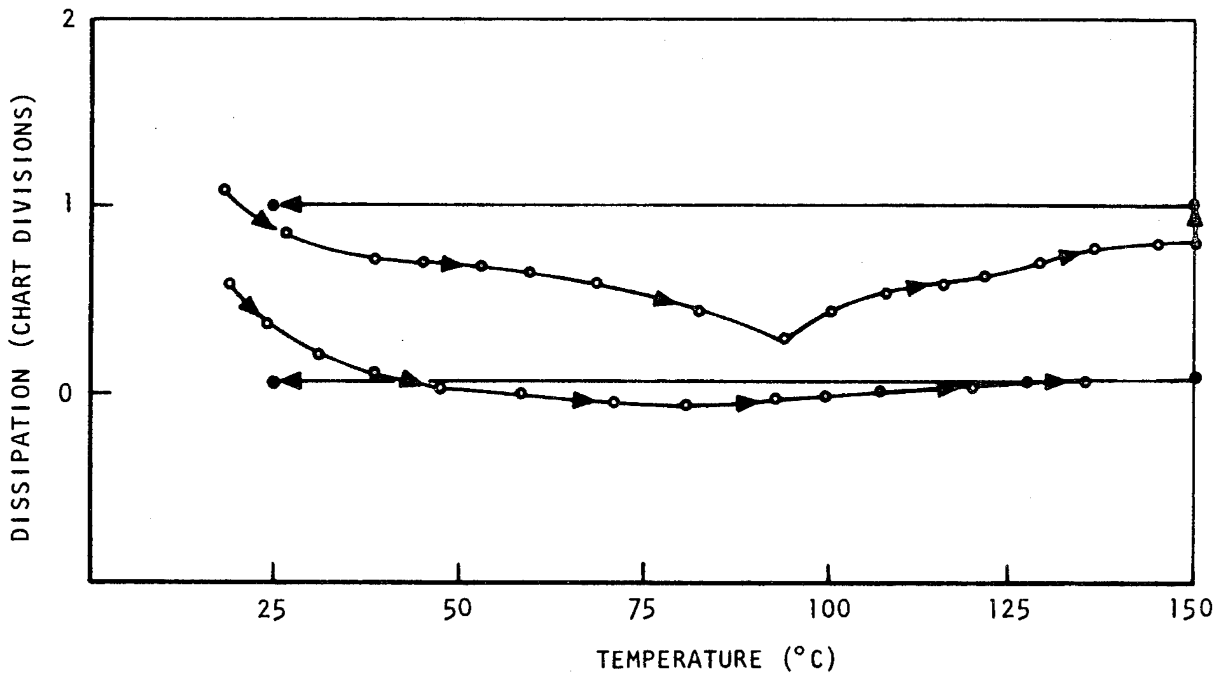

Figure 4. Nonlinear Dissipation in Chart Divisions as a Function of Temperature in°C for BR-125 Adhesive Primer